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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03405420.5

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 03405420.5
Demande no:

Anmeldetag:
Date of filing: 11.06.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

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SUISSE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Storage-stable fluorescent whitener formulations

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/ Classification internationale des brevets:

C11D/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

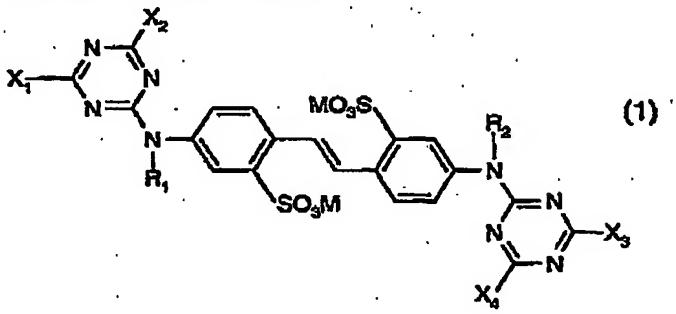
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL PT RO SE SI SK TR LI

Storage-stable fluorescent whitener formulations

The present invention relates to storage-stable fluorescent whitener formulations, a process for their preparation and their use.

The storage-stable fluorescent whitener formulations according to the invention accordingly have a content of

(a) 5 – 60% by weight, based on the total weight of the whitener formulation, of at least one compound of formula (1)



(1)

wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1-C_8alkyl,

X_1, X_2, X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen, cyano, unsubstituted or substituted C_1-C_8alkyl or C_5-C_7cycloalkyl, or R_3 and R_4, together with the nitrogen atom linking them, form a heterocyclic ring, and R_5 is unsubstituted or substituted C_1-C_8alkyl, and

M is hydrogen or a cation,

(b) 0.01 – 1 % by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide,

(c) 0 – 25% by weight, based on the total weight of the whitener formulation, of at least one electrolyte,

(d) 0 – 20 % by weight, based on the total weight of the whitener formulation, of at least one dispersant,

(e) 0 – 30 % by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener,

(f) 0 – 5 % by weight, based on the total weight of the whitener formulation, of at least one further optional component, and

(g) water to make up 100% by weight.

These novel formulations are suspensions, and are stable for several months even at elevated temperatures.

Within the scope of the above definitions, C_1-C_8alkyl may be methyl, ethyl, n- or isopropyl, n-, sec.- or t-butyl, or linear or branched pentyl, hexyl, heptyl or octyl. Preferred are C_1-C_4alkyl groups. In case the alkyl groups are substituted examples of possible substituents are hydroxyl, halogen, like fluorine, chlorine or bromine, sulfo, sulfato, carboxy and C_1-C_4alkoxy, like methoxy and ethoxy. Other substituents of such alkyl groups are, for example, cyano, $-CONH_2$ and phenyl. Preferred substituents are hydroxy, carboxy, cyano, $-CONH_2$ and phenyl, especially hydroxy and carboxy. Furthermore, highly preferred substituents are hydroxy and C_1-C_4alkoxy, especially hydroxy. The alkyl groups can also be uninterrupted or interrupted by –O- (in case of alkyl groups containing two or more carbon atoms).

Examples for C_5-C_7cycloalkyl groups are cyclopentyl and especially cyclohexyl. These groups can be unsubstituted or substituted by, for example, C_1-C_4-alkyl, like methyl. Preferred are the corresponding unsubstituted cycloalkyl groups.

Within the scope of the above definitions, C_1-C_8alkoxy may be methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy, tert.-butoxy, or linear or branched higher alkoxy groups. Preferred are C_1-C_4alkoxy groups, especially methoxy or ethoxy. Highly preferred is methoxy.

Halogen may be fluorine, chlorine, bromine or iodine, preferably chlorine.

If R_3 and R_4 together with the nitrogen atom form a heterocyclic ring such a ring system can be, for example, morpholino, piperidine or pyrrolidine. The heterocyclic ring can be unsubstituted or substituted. An example for such substituents is C_1-C_4alkyl, especially methyl.

The cation M is preferably an alkali metal atom, an alkaline earth metal atom, ammonium or a cation formed from an amine. Preferred are Li, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_2-C_4-hydroxyalkylammonium or ammonium

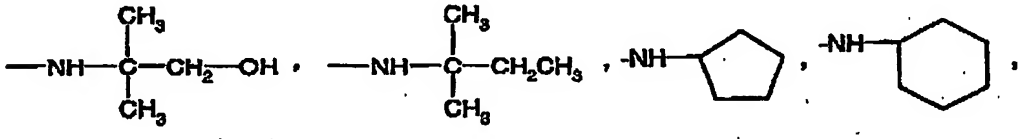
that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_2-C_4-hydroxyalkyl groups. Highly preferred is sodium.

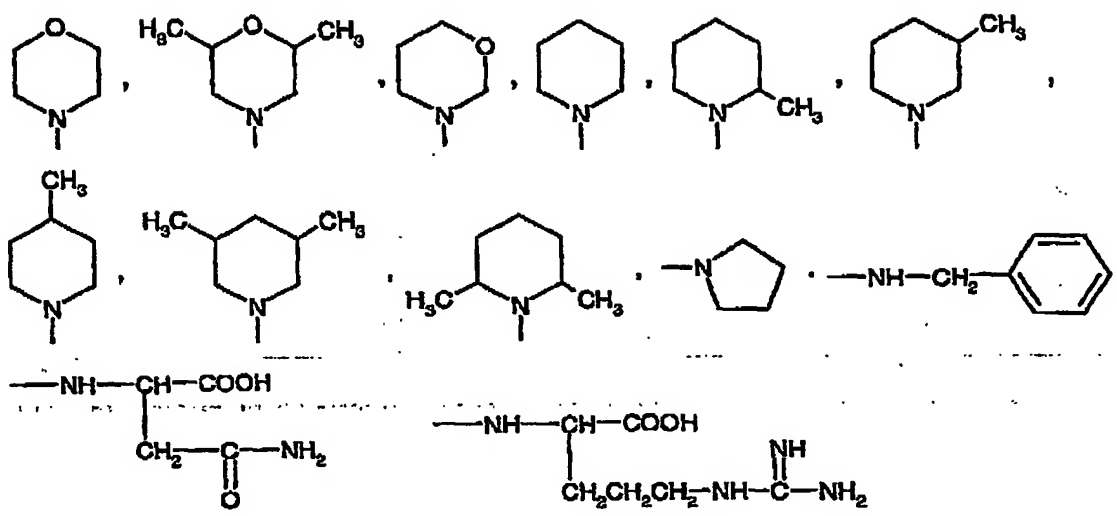
R_1 and R_2 are preferably hydrogen or C_1-C_4alkyl, especially hydrogen.

R_3 and R_4 are preferably hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl, especially by hydroxy or carboxy, and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by –O-; unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl, especially cyclohexyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

More preferably, R_3 and R_4 are hydrogen, unsubstituted or hydroxy-substituted C_1-C_8alkyl, unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl, or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring. Highly preferred meanings for R_3 and R_4 are hydrogen, unsubstituted or hydroxy-substituted C_1-C_8alkyl, or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring. Most preferred are unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine rings, especially morpholino, formed by R_3 and R_4 together with the nitrogen atom linking them.

Examples of $-N(R_3)R_4$ groups are $-NH_2$, $-NHCH_3$, $-NHC_2H_5$, $-NH(n\text{-}C_3H_7)$, $-NH(i\text{-}C_3H_7)$, $-NH(i\text{-}C_4H_9)$, $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N(i\text{-}C_3H_7)_2$, $-NH(CH_2CH_2OH)$, $-N(CH_2CH_2OH)_2$, $-N(CH_2CH(OH)CH_3)_2$, $-N(CH_3)(CH_2CH_2OH)$, $-N(C_2H_5)(CH_2CH_2OH)$, $-N(i\text{-}C_3H_7)(CH_2CH_2CH_2OH)$, $-NH(CH_2CH(OH)CH_3)$, $-N(C_2H_5)(CH_2CH(OH)CH_3)$, $-NH(CH_2CH_2OCH_3)$, $-NH(CH_2CH_2OCH_2CH_2OH)$, $-NH(CH_2COOH)$, $-NH(CH_2CH_2COOH)$, $-N(CH_3)(CH_2COOH)$, $-NH(CN)$,





R_5 is preferably C_1-C_8alkyl, especially C_1-C_4alkyl, which is unsubstituted or substituted by C_1-C_4alkoxy or especially hydroxy. Highly preferred for R_5 is methyl or ethyl, especially methyl.

X_1, X_2, X_3 and X_4 are preferably a radical of formula $-N(R_3)R_4$.

X_1 and X_3 have preferably the same meanings. In addition it is preferred that X_2 and X_4 have preferably the same meanings. Furthermore, it is preferred that the four radicals X_1, X_2, X_3 and X_4 do not have identical meanings.

Preferred are compounds of formula (1), wherein
R_1 and R_2 are hydrogen or C_1-C_4alkyl,
R_3 and R_4 are hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by –O–; unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring; and
R_5 is C_1-C_8alkyl which is unsubstituted or substituted by hydroxy.
As to R_3, R_4 and R_5 the above preferences apply.

Highly preferred are compounds of formula (1), wherein
X_1 and X_3 are amino, and

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein R_3 and R_4 are hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by –O-; unsubstituted or C_1-C_4alkyl-substituted cyclohexyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.
As to R_3 and R_4 the above preferences apply.

Of particular interest are compounds of formula (1), wherein X_1 and X_3 are amino, and X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein R_3 and R_4 are hydrogen, unsubstituted or hydroxy-substituted C_1-C_8alkyl, unsubstituted or C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl, or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring. Most interesting compounds of formula (1) are those wherein R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring. As to R_3 and R_4 the above preferences apply.

The amount of the compound(s) of formula (1) can be 5 to 60% by weight, preferably 5 to 50% by weight, more preferably 10 to 50% by weight, particularly preferably 10 to 45% by weight, based on the total weight of the formulation.

The compounds of formulae (1) are known or can be prepared in analogy to known processes.

Compounds of formula (1) may be produced by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'- disulfonic acid, and amino compounds capable of introducing the groups X_1, X_2, X_3 and X_4. Preferably, 2 moles of cyanuric chloride are initially reacted with 1 mole of 4,4'-diaminostilbene-2,2'- disulfonic acid and then reacting the intermediate obtained in any order with amino compounds capable of introducing the groups X_1, X_2, X_3 and X_4. For the preparation of compounds wherein X_1 and X_3 having the same meaning, and also X_2 and X_4 have the same meaning, it is preferred to react the intermediate obtained first with an amino compound capable of introducing X_1 and X_3, and, finally with an amino compound capable of introducing X_2 and X_4. It is also possible to carry out the reaction with the amino

compounds in one step by reacting the intermediate with a mixture of amino compounds; in such a case usually corresponding mixtures of compounds of formula (1) are obtained.

Compounds of formula (1) containing a radical of formula $-OR_5$ can for example be prepared by first reacting cyanuric chloride with the corresponding alcohol HOR_5, reacting the product obtained with 4,4'-diaminostilbene-2,2'- disulfonic acid and then reacting the intermediate with further compounds capable of introducing the remaining groups of X_1, X_2, X_3 and X_4. The last reaction is preferably carried out with the corresponding amines.

The anionic polysaccharides which can be used according to the invention belong to the group of modified polysaccharides which can be derived from cellulose, starch or the heteropolysaccharides, it being possible for the side chains to contain further monosaccharides, for example mannose and glucuronic acid. Examples of anionic polysaccharides are sodium alginate, carboxymethylated guar, carboxymethylcellulose, carboxymethyl-starch, carboxymethylated locust bean flour and, particularly preferably, xanthan gum.

The amount of polysaccharide is 0.01 to 1% by weight, a range from 0.05 to 0.5% by weight being preferred and a range of 0.1 to 0.3% by weight being particularly preferred, in each case based on the total weight of the formulation. However, these ranges can be exceeded in formulations of very high concentration or very low concentration.

One or more alkali metal salts and salts of lower carboxylic acids, for example, can be used as the electrolyte. Examples of electrolytes are sodium chloride, sodium sulfate, sodium phosphate, sodium carbonate, sodium formate, sodium citrate or one of the corresponding potassium salts, and mixtures of these electrolytes. Sodium chloride, sodium citrate and the formates are preferred here. The amount of electrolyte can be 0 to 25% by weight, preferably 0.5 to 20% by weight and particularly preferably 0.5 to 15% by weight, based on the total weight of the formulation.

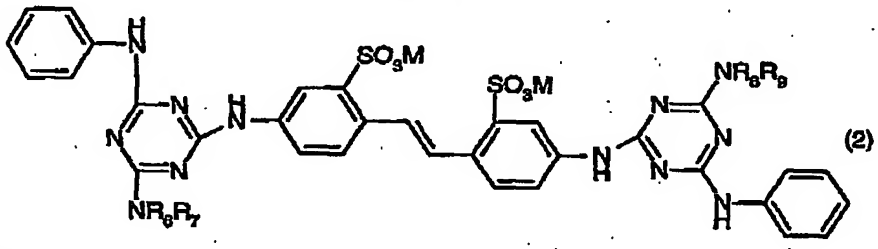
Dispersants which can be used are those of the anionic or nonionic type. Examples of these are alkylbenzenesulfonates, alkyl or alkenyl ether-sulfonate salts, saturated or unsaturated fatty acids, alkyl or alkylene ether-carboxylic salts, sulfo-fatty acid salts or esters, phosphate esters, polyoxyethylene alkyl or alkenyl ethers, polyoxyethylene alkylvinyl ethers,

polyoxypropylene alkyl or alkenyl ethers, polyoxybutylene alkyl or alkenyl ethers, higher fatty acid alkanolamides or alkylene oxide adducts, sucrose/fatty acid esters, fatty acid/glycol monoesters, alkylamine oxides and condensation products of aromatic sulfonic acids with formaldehyde, and lignin-sulfonates, or mixtures of the abovementioned dispersants. The condensation products of aromatic sulfonic acids with formaldehyde, and lignin-sulfonates are preferred. Condensation products of naphthalenesulfonic acids with formaldehyde and of ditolyl ether-sulfonic acids with formaldehyde are particularly preferred.

The content of dispersant is 0 to 20% by weight, based on the total weight of the formulation, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, particularly preferably 0.2 to 5% by weight.

The storage-stable fluorescent whitener formulations according to the invention can further comprise

0 – 30 % by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener of formula (2) .



(2)

wherein

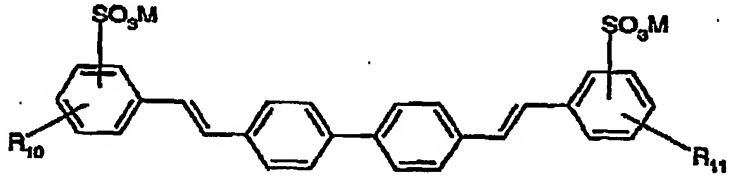
R_8 and R_7, independently from each other, are hydrogen, unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl,

R_8 and R_9, independently from each other, are hydrogen, unsubstituted phenyl; unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl, or

NR_8R_7 and/or NR_8R_9 form a morpholino ring,

and M is hydrogen or a cation,

and/or of at least a further fluorescent whitener of formula (3)



(3),

wherein

R_{10} and R_{11}, independently of each other, are hydrogen, C_1-C_8alkyl, C_1-C_8alkoxy or halogen, and M is hydrogen or a cation.

Preferred compounds of formula (2) are those wherein

R_3 and R_5, independently of each other, are hydrogen; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl,

R_4 and R_6, independently of each other, are unsubstituted phenyl; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl, or

NR_3R_4 and/or NR_5R_6 form a morpholino ring,

and M is an alkali metal atom, an alkaline earth metal atom, ammonium or a cation formed from an amine.

More preferred compounds of formula (2) are those wherein

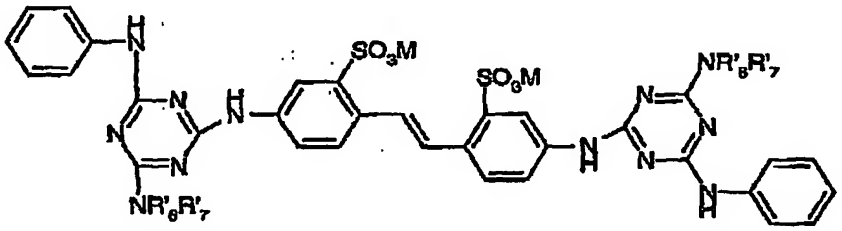
R_8 and R_8, independently of each other, are hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,

R_7 and R_9, independently of each other, are unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or

NR_8R_7 and/or NR_8R_9 form a morpholino ring,

and M is an alkali metal atom.

Especially preferred compounds of formula (2) are those of formula (2a)



(2a)

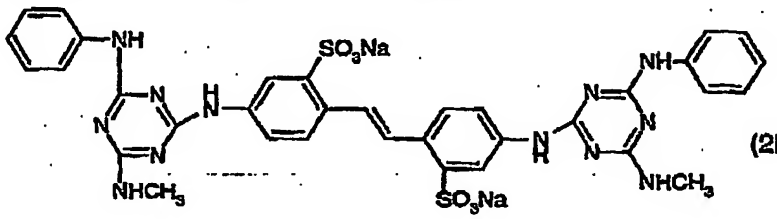
wherein

R'_8 is hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,

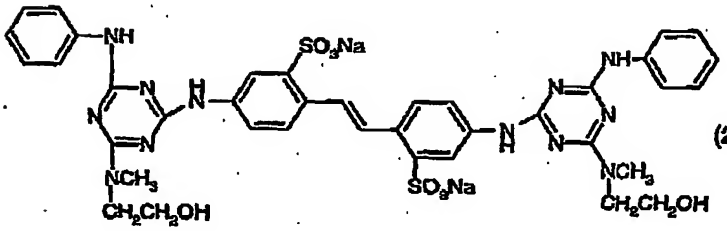
R'_7 is unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or

$NR'_8R'_7$ forms a morpholino ring,
and M is an alkali metal atom, preferably sodium.

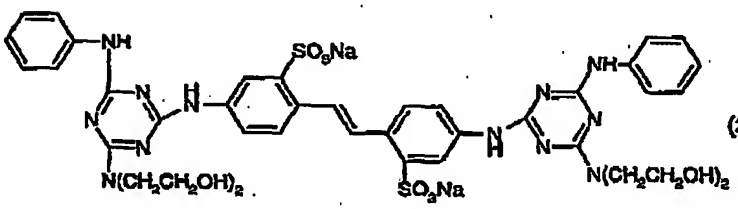
Example of such preferred compounds of formula (2) are those of formula (2b) – (2f)



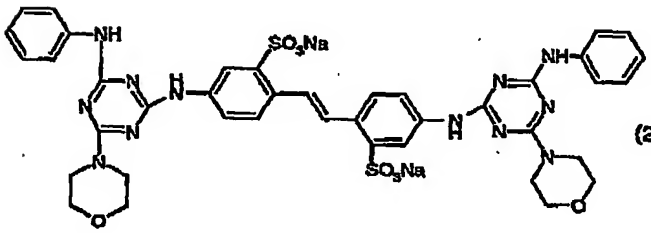
(2b)



(2c)

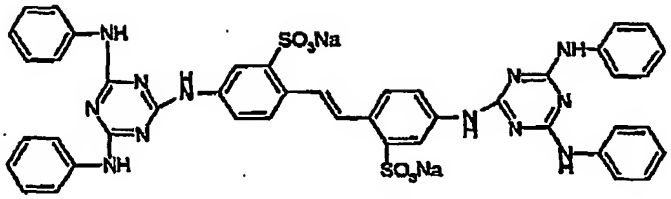


(2d)



(2e)

and



(2f)

Preferred compounds of formula (2) are those wherein
R_{10} and R_{11}, independently of each other, are hydrogen, C_1-C_4alkyl, C_1-C_4alkoxy or halogen, and M is hydrogen or a cation.

Compounds of formula (2) and (3) as well as their process of production are known.

In the mixtures of compounds of formulae (1) and (2) and/or (3) the molar ratio of compound (1) to compound (2) and/or compound (3) is usually in the range of from 0.1:99.9 to 99.9:0.1, preferably from 1:99 to 99:1 and more preferably from 5:95 to 95:5. Highly preferred is a molar ratio of from 10:90 to 90:10, especially 20:80 to 80:20. Most important is a molar ratio of from 30:70 to 70:30, especially 40:60 to 60:40.

If appropriate, the whitener formulation according to the invention can further comprise optional components; examples are preservatives or mixtures of preservatives, such as chloroacetamide, triazine derivates, benzoisothiazolines, 2-methyl-2H-isothiazol-3on, 2-octyl-2H-isothiazol-3on, 2-brom-2-nitropropan-1,3-diol or aqueous formaldehyde solution; Mg/Al silicates or mixtures of Mg/Al silicates, such as bentonite, montmorillonite, zeolites or highly disperse silicic acids; odour improvers and perfuming agent or mixtures thereof; antifoam agents or mixtures thereof; builders or mixtures thereof; protective colloids or mixtures thereof; stabilizers or mixtures thereof; sequestering agents and antifreeze agents or mixtures thereof, such as propylene glycol.

The content of these optional components is 0 to 20% by weight, based on the total weight of the formulation, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, particularly preferably 0.2 to 5% by weight.

Examples of suitable builders or protective colloids are modified polysaccharides derived from cellulose or heteropolysaccharides, such as xanthan gum, carboxymethylcellulose and

polyvinyl alcohols (PVA), polyvinylpyrrolidones (PVP), polyethylene glycols (PEG) and aluminium silicates or magnesium silicates. They are usually used in a concentration range of 0.01 to 2% by weight and preferably 0.05 to 0.5% by weight, based on the total weight of the formulation.

Examples of auxillaries which can be used for stabilization are ethylene glycol, propylene glycol or dispersants in an amount of 0.2 to 5% by weight and preferably 0.3 to 2% by weight, based on the total weight of the formulation.

Compounds which are used as preservatives are chloroacetamide, triazine derivates, benzoisothiazolines, 2-methyl-2H-isothiazol-3on, 2-octyl-2H-isothiazol-3on, 2-brom-2-nitropropan-1,3-diol or aqueous formaldehyde solution in an amount of 0.1 to 1% by weight and preferably 0.1 to 0.5% by weight based on the total weight of the formulation.

The storage-stable formulations of this invention are prepared by mixing the moist filter cake or also the dry powder, which comprises at least one fluorescent whitening agent of formula (1) in an amount of 5 - 60% by weight, based on the total weight of the formulation, with 0.01-1% by weight of an anionic polysaccharide and water, and homogenising the formulations.

The desired content of anionic fluorescent whitening agent in the suspension can be adjusted either by addition of water, aqueous electrolyte, suspension, further fluorescent agent(s) of formulae (2) and/or (3) or further dry powder to the moist filter cake. This adjustment can be made before, during or after addition of the anionic polysaccharide.

The concentrated formulation thus prepared can be used for the fluorescent whitening of paper or textile material, for example in detergents. To this end, they are in general diluted to the optimum concentration for the practical application by the addition of further components or water.

The novel storage-stable fluorescent whitener formulations are used in particular for incorporation into washing agents, for example by allowing the required amount of the fluorescent whitener formulation according to the invention to run from a tank into a mixing device which contains a suspension of the washing agent or the dispersant.

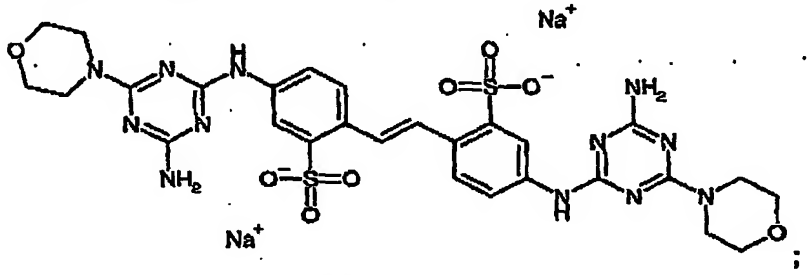
The present invention accordingly also relates to a process for the preparation of solid and liquid washing agents, and to the washing agents obtained by this process, which comprises mixing, for example, a suspension of detergents customary for washing agents with a suspension, according to the invention, of whiteners, and drying the mixture. The drying procedure here can be carried out by, for example, a spray-drying method.

The following examples illustrate the invention, without limiting it thereto. Percentage data relate to the total weight of the formulation.

EXAMPLE 1

With stirring, the components listed below are mixed and homogenised at 20°C:

30.0% by weight of the fluorescent whitening agent of formula



;

0.5% by weight of propylene glycol;

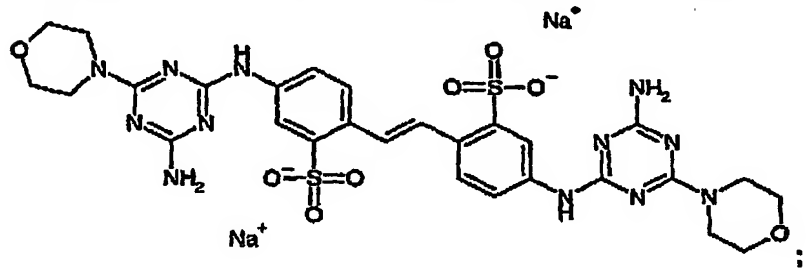
0.25% by weight of Xanthan,

0.4% by weight of Acticide MBS® (Trade name of Acti-Chem Specialties Inc.) and deionised water to make up 100%.

EXAMPLE 2

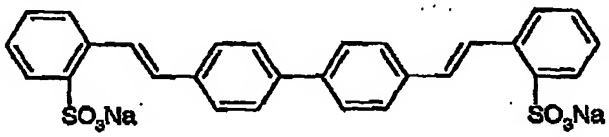
With stirring, the components listed below are mixed and homogenised at 20°C:

11.1% by weight of the fluorescent whitening agent of formula



;

18.9% by weight of the fluorescent whitening agent of formula

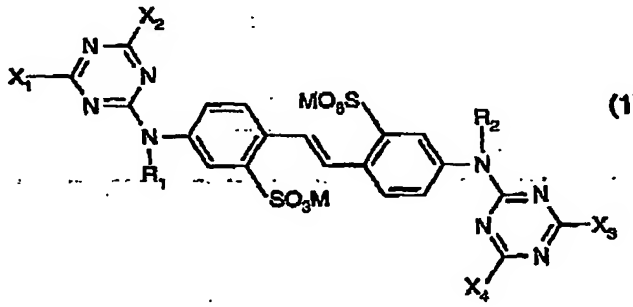


0.5% by weight of propylene glycol;
0.25% by weight of Xanthan,
0.4% by weight of Acticide MBS® (Trade name of Acti-Chem Specialties Inc.)
0.001% by weight of Surfynol 104 PG 50® (Trade name of Air Products and Chemicals Inc.)
and deionised water to make up 100%.

Claims

1. A storage-stable fluorescent whitener formulation comprising

(a) 5 – 60% by weight, based on the total weight of the whitener formulation, of at least one compound of formula



(1)

wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1-C_8alkyl,

X_1, X_2, X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen, cyano, unsubstituted or substituted C_1-C_8alkyl or C_5-C_7cycloalkyl, or R_3 and R_4, together with the nitrogen atom linking them, form a heterocyclic ring, and R_5 is unsubstituted or substituted C_1-C_8alkyl, and

M is hydrogen or a cation,

(b) 0.01 – 1 % by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide,

(c) 0 – 25% by weight, based on the total weight of the whitener formulation, of at least one electrolyte,

(d) 0 – 20 % by weight, based on the total weight of the whitener formulation, of at least one dispersant,

(e) 0 – 30 % by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener,

(f) 0 – 5 % by weight, based on the total weight of the whitener formulation, of at least one further optional component, and

(g) water to make up 100% by weight.

2. A storage-stable fluorescent whitener formulation according to claim 1 comprising 5 – 60% by weight, based on the total weight of the whitener formulation, of at least

one compound of formula (1), wherein
R_1 and R_2 are hydrogen or C_1-C_4alkyl,
R_3 and R_4 are hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, -$CONH_2$ or phenyl and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by –O-; unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring; and
R_5 is C_1-C_8alkyl which is unsubstituted or substituted by hydroxy.

3. A storage-stable fluorescent whitener formulation according to claim 1 comprising
5 – 60% by weight, based on the total weight of the whitener formulation, of at least one compound of formula (1), wherein
X_1 and X_3 are amino, and
X_2 and X_4 are a radical of formula -$N(R_3)R_4$, wherein R_3 and R_4 are hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by –O-; unsubstituted or C_1-C_4alkyl-substituted cyclohexyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

4. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising
5 to 50% by weight, preferably 10 to 50% by weight, based on the total weight of the formulation, of at least one compound of formula (1).

5. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims wherein the anionic polysaccharide is selected from the group consisting of sodium alginate, carboxymethylated guar, carboxymethylcellulose, carboxymethyl-starch, carboxymethylated locust bean flour and xanthan gum.

6. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising
0.05 to 0.5% by weight, preferably 0.1 to 0.3% by weight, based on the total weight of the formulation, of at least one anionic polysaccharide.

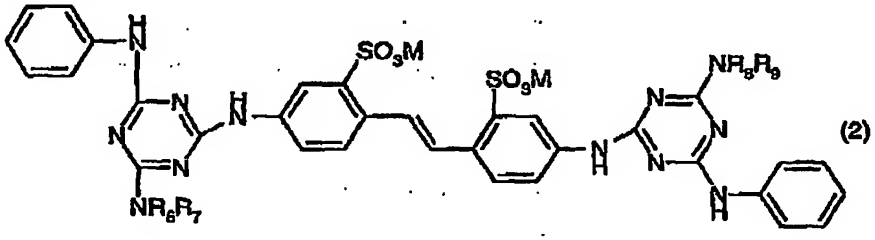
7. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims wherein the electrolyte or the mixture of electrolytes are selected from the group consisting of alkali metal salts and salts of lower carboxylic acids.

8. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising
0.5 to 20% by weight, preferably 0.5 to 15% by weight, based on the total weight of the formulation, of at least one electrolyte.

9. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims wherein the dispersant or the mixture of dispersants are selected from the group consisting of alkylbenzenesulfonates, alkyl or alkenyl ether-sulfonate salts, saturated or unsaturated fatty acids, alkyl or alkylene ether-carboxylic salts, sulfo-fatty acid salts or esters, phosphate esters, polyoxyethylene alkyl or alkenyl ethers, polyoxyethylene alkylvinyl ethers, polyoxypropylene alkyl or alkenyl ethers, polyoxybutylene alkyl or alkenyl ethers, higher fatty acid alkanolamides or alkylene oxide adducts, sucrose/fatty acid esters, fatty acid/glycol monoesters, alkylamine oxides and condensation products of aromatic sulfonic acids with formaldehyde and lignin-sulfonates.

10. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising 0.1 to 20% by weight, preferably 0.1 to 10% by weight, based on the total weight of the formulation, of at least one dispersant.

11. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising of at least one further fluorescent whitener of formula (2)



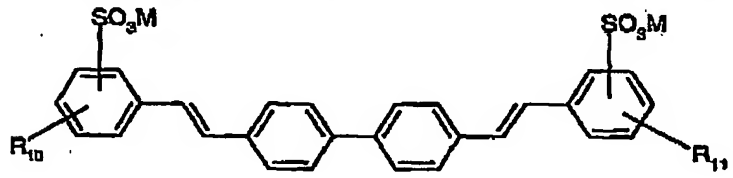
(2)

wherein
R_6 and R_7, independently from each other, are hydrogen, unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl,

R_8 and R_9, independently from each other, are hydrogen, unsubstituted phenyl; unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl, or
NR_6R_7 and/or NR_8R_9 form a morpholino ring,
and M is hydrogen or a cation.

12. A storage-stable fluorescent whitener formulation according to claim 11 wherein
R_3 and R_5, independently of each other, are hydrogen; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl,
R_4 and R_6, independently of each other, are unsubstituted phenyl; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl, or
NR_3R_4 and/or NR_5R_6 form a morpholino ring,
and M is an alkali metal atom, an alkaline earth metal atom, ammonium or a cation formed from an amine.

13. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising of at least one further fluorescent whitener of formula (3)



(3),

wherein
R_{10} and R_{11}, independently of each other, are hydrogen, C_1-C_8alkyl, C_1-C_8alkoxy or halogen, and M is hydrogen or a cation.
More preferred compounds of formula (2) are those wherein
R_3 and R_5, independently of each other, are hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,
R_7 and R_9, independently of each other, are unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or
NR_6R_7 and/or NR_8R_9 form a morpholino ring,
and M is an alkali metal atom.

14. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising 0 to 25 % by weight, preferably 0 to 20 % by weight, of at least one further fluorescent whitener of formula (2) and/or formula (3).

15. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims wherein optional components are selected from the group consisting of preservatives; Mg/Al silicates; odour improvers; perfuming agent; antifoam agents; builders; protective colloids; stabilizers; sequestering agents and antifreeze agents.

16. A storage-stable fluorescent whitener formulation according to anyone of the preceding claims comprising 0.1 to 20% by weight, preferably 0.1 to 10% by weight, particularly preferably 0.2 to 5% by weight based on the total weight of the formulation, of at least one optional component.

17. A process for the preparation of a storage-stable fluorescent whitener formulation according to any one of the preceding claims, which comprise mixing the moist filter cake or the dry powder of the fluorescent whitening of formula (1) with least one anionic polysaccharide and water, and homogenizing the formulation.

18. The use of a storage-stable fluorescent whitener formulation according to any one of claim 1 – 16 for the preparation of a detergent composition.

Abstract

The present invention relates to storage-stable fluorescent whitener formulations, a process for their preparation and their use.